

ELECTRIC OSMOSE

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

BY

HARRY N. HOLMES

BALTIMORE

1907

EASTON, PA. :
ESCHENBACH PRINTING COMPANY.
1907.

ELECTRIC OSMOSE

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

BY

HARRY N. HOLMES

BALTIMORE

1907

EASTON, PA. :
ESCHENBACH PRINTING COMPANY.
1907.



CONTENTS.

	PAGE.
Acknowledgment	4
Definition of Electric Osmose.	5
Historical preface.	5
Theories advanced.	8
Preliminary experiments of Frazer.	10
Description of apparatus	
1. Drainage form.	12
2. Frazer form.	16
Methods of working.	19
Tabulation of results.	23
Movement of colloidal particles.	27
Electrostenolysis	27
Discussion of results.	28
Appendix	30
Biographical	32

ACKNOWLEDGMENT.

The author takes pleasure in expressing his gratitude to President Remsen, Professor Morse, Professor Jones and Professor Ames for instruction received from them, and especially to Dr. Frazer, under whose direction this investigation has been pursued, for guidance in the work and for his personal interest.

Thanks are also due to Professor Bliss, Professor Renouf, Dr. Tingle and Dr. Acree for instruction and suggestions.

ELECTRIC OSMOSE.

If a vessel divided into two compartments by means of a porous partition be filled with a solution of an electrolyte and an electric current passed through the solution we shall find a transfer of the liquid through the porous wall, usually in the direction of the current.

HISTORICAL PREFACE.

The phenomenon of electric osmose was first observed by Reuss¹ in Moscow in 1807. A few years later Porret² gave some attention to the subject without adding anything to the observations of Reuss.

Since that time a considerable number of investigators have studied the phenomenon and of these Wiedeman and Quincke contributed most of the experimental data, elaborated mathematically by Helmholtz.

Reuss, in his original experiments, placed sand and clay in the bend of a U tube, filled the tube with water, set platinum electrodes in the two arms, and on passing a current of electricity through the tube, observed a rise in the level of the water in the arm containing the cathode. Reuss named the phenomenon "Motus stoechiagogus." E. du Bois-Raymond referred to it as "Kataphorische Wirkung des Stromes," but the term now used is "Electric Osmose."

To measure osmose, Wiedeman³ used an apparatus consisting, in part, of a porous clay cell open at the top and containing a platinum cathode. The cell was surrounded by the anode and placed in a larger glass vessel, both cell and glass vessel being filled with the solution. A glass tube was sealed to the top of the porous cell and, extending vertically a short distance, was bent at a right angle, the open end situated just

¹ Mémoires de la soc. imp. des naturalistes a Moscou, II, 327 (1807).

² Thomson's Jour., July, 1816.

³ Pogg. Ann., 87, 321 (1852); *Ibid.*, 99, 177 (1856); Wied. Elect., II, 166.

above a weighing-bottle. On passing a current from anode to cathode the liquid rose in the porous cell and the vertical tube, flowed into the weighing-bottle, and was weighed.

In another series of measurements this same form of apparatus was connected with a manometer and the pressure recorded instead of weighing the liquid drawn in as was done in the first series.

In each series the opposing hydrostatic pressure introduced large errors.

Wiedeman and Quincke¹ experimented with the movement of a liquid through a narrow glass tube when driven by the electric current. In their opinion this was equivalent to selecting a single pore of any porous membrane. In other words they experimented with a single capillary and also a system of capillaries such as any porous wall.

Engelmann² tried the effect of different membranes on osmose and found marked variations with porous clay, thin slice of potato, parsnip, frogskin, pig's bladder and cat's lung. The apparatus he used consisted, in part, of two glass vessels, in each of which a glass tube was sealed around an opening in one side. The outer ends of these tubes were connected with a block of hard rubber through which a hole was bored connecting the outer ends of the glass tubes above mentioned. This hole through the block was tapped by another hole entering from above. In the latter was set a vertical glass tube.

To measure the effect of different membranes, Engelmann inserted two membranes between the rubber block and the outer ends of the glass tubes leading to the glass vessels. A platinum electrode was placed in each of these vessels and the whole apparatus filled with solution. When the current was passed between the electrodes the liquid moved from one vessel to the other but if one membrane allowed greater osmose than the other the liquid rose in the vertical tube, depending on the direction of the electric current. This was a rather delicate method of showing variations in osmose through different kinds of membranes.

¹ Pogg. Ann., 113, 513 (1861).

² Arch. Neerland, 9, 332 (1874).

Engelmann was the first to point out the importance of electrolyzing the solution only a very short time. He stated that this precaution was to allow the separation of ions from solution to have as little influence as possible.

Quincke's¹ elaborate experiments were of the utmost importance and furnished the material for Helmholtz' theory of osmose.

Quincke worked with distilled water and solutions of salts and acids, but found that addition of a salt or acid to the water decreased the osmose. However, his distilled water was far from being conductivity water as now prepared and the salt solutions were quite concentrated in comparison with $\frac{N}{1000}$ solutions. Working with capillary and other tubes he found that the osmose varied inversely as the fourth power of the diameter of the tubes.

If the inner part of the glass tube were coated with shellac the flow of water was greater than over glass. On the other hand, a silver tube gave less osmose with water than a similar glass tube.

Alcohol, he states, gave less osmose in glass tubes than did water.

Although in most cases the liquid moved with the current of electricity he found that turpentine flowing over glass or shellac surface moves in the opposite direction, that is, toward the anode. Yet if the tube were lined with sulphur the turpentine flowed with the electric current.

Practically, the same fact was shown in another way. A porous clay wall was cemented in a glass tube and in a similar tube a sulphur wall was fixed. The flow of turpentine due to the electric current was in opposite directions in the two tubes.

Carbon bisulphide was found to flow in the same direction as the electric current except in the case of one peculiar glass tube.

Wiedemann and Quincke each state that osmose in equal times is directly proportional to the intensity of the electric current and, under like conditions, independent of the area or

¹ Pogg. Ann., 113, 513 (1861).

thickness of the porous wall. For these experiments Wiedemann used a vessel divided into three compartments by two porous clay walls of different area or thickness. In the two outer compartments were placed the electrodes. When the apparatus was filled with solution and the current turned on, the level of the liquid in the middle compartment remained the same irrespective of difference in the area or thickness of the two clay walls. This work clearly showed that area or thickness of a porous membrane has no influence on osmose.

Freund¹ found that with zinc sulphate solutions the osmose varied nearly inversely as the concentration. His solutions seem to have been in the neighborhood of normal.

Gore² speaks of a negative osmose with alcoholic solution of barium bromide. He tested sixty-seven substances and found osmose with all except potassium cyanide.

THEORIES ADVANCED.

Raoult's³ theory assumes the formation of compounds by the products of electrolysis and the solvent with a consequent change in volume.

Weiske's⁴ theory is based on the assumption of an accumulation of electricity at the surface of contact of the electrolyte and the electrode. The less the electrolyte conducts, the more important is this accumulation. The cation is a better conductor than the anion. When the good conducting cation goes to the cathode it takes a negative charge from that electrode which spreads over the surface of the other cations, leaving no charge on the cathode. In the case of the anions they take a positive charge at the surface of contact with the anode, but this charge does not spread further over the poor conducting anions and so the solution is driven to the negative electrode. This theory is far from clear.

¹ Wied. Ann., 7, 51 (1879).

² Proc. Roy. Soc., 31, 253 (1880).

³ Compt. rend., 36, 826 (1853).

⁴ Pogg. Ann., 103, 466 (1858).

Mattenci¹ considered osmose as a phenomenon quite separate from electrolysis.

Quincke considers osmose as an electro-capillary phenomenon depending on natural potential differences at the surface of separation of two unlike substances—an electrolyte and an insulator. In the case of an aqueous solution in a porous clay wall there is a difference of potential between the water and the clay wall of each capillary pore. The film of water next the clay wall is positively electrified and is attracted to the negative electrode during the passage of the current, dragging with it more water. The smaller the pore, of course, the greater the amount of water is dragged through. This potential difference Helmholtz believed to be of the order of one volt. Helmholtz² gave mathematical expression to Quincke's theory. He demonstrated by formula that electric osmose varies directly as the specific resistance of the solution, in addition to the laws previously mentioned. The experimental evidence to which he referred was largely qualitative.

Shaw³ suggests that osmose is an essential feature of the mechanism of electrolysis, the motion of the liquid being due to the drift of complex ions made up of an ion of the salt attached to a large number of solvent molecules.

Whetham⁴ thinks that the inverse proportionality between the concentration of the solution and the osmose shows that in very dilute solution such complex ions must contain many hundreds or even thousands of molecules, but considers the phenomenon as not directly connected with the electrolytic process.

There is no record of any further work on the subject until 1905 when Frazer undertook to devise an efficient apparatus for the quantitative determination of osmose.

Only a few days' time was given to the experiments and several factors interfered with the accuracy of the work. The conductivity water used was exceedingly poor, salts were not dried with the greatest care and the drainage through the outlet

¹ Compt. rend., 51, 914 (1860).

² Wied. Ann., 7, 351 (1879).

³ B. A. Report, 202 (1890).

⁴ Whetham's Theory of Sol., 292

tubes was not as regular as has since been secured. The lack of time also necessitated the use of vessels, one of which contained nearly a half more liquid than the other. This magnified the errors due to the different rates of electrolysis. The drainage tubes were not kept clean and no precautions were taken to keep dust out of the apparatus—a factor that in later experiments with the original cells reduced their osmose so much as to cause the experimenters to secure new and clean cells.

To make drainage more regular a short platinum wire bent in U shape rested on the upper end of the drainage tubes, the bend hanging within the tubes, and the two arms on the upper edge. This device was insufficient because of the limited number of points of contact and difficulty of keeping the platinum rider in a fixed position.

With the five salts used only six tests were made but the amount of osmose—in spite of errors—was not proportional to the specific resistance in solutions of various electrolytes as deduced by Helmholtz.¹

In these preliminary experiments Frazer used $\frac{N}{1000}$ aqueous solutions of different nitrates, and selected the osmose of $\frac{N}{1000}$ potassium nitrate as the standard of comparison. Below is given the osmose of the five salts tested, expressing the osmose of potassium nitrate as one hundred.

$\text{KNO}_3 = 100$	$1/2 \text{ Sr}(\text{NO}_3)_2 = 72$
$\text{NaNO}_3 = 119$	$1/2 \text{ Ba}(\text{NO}_3)_2 = 61$
$\text{NaNO}_3 = 120$	$1/2 \text{ Ba}(\text{NO}_3)_2 = 65$
$\text{LiNO}_3 = 151$	

A comparison of these values with the relative specific resistances in the following tables made a series of accurate measurements desirable. As previously stated, Helmholtz demonstrated mathematically that osmose should vary as the specific resistance of the solution.

The following values are given for $\frac{N}{1000}$ solutions at 18° and

¹ Wied. Ann., 7, 351 (1879).

are calculated from "Leitvermögen der Electrolyte" by Kohlrausch and Holborn.

	Relative specific resistance.	Molecular conductivity.	Specific resistance.
KNO_3	100	122.9	8136
NaNO_3	120.8	101.8	9823
LiNO_3	139.7	88.	11363
$1/2 \text{ Ba}(\text{NO}_3)_2$	109.	112.8	8865
$1/2 \text{ Sr}(\text{NO}_3)_2$	114.4	107.5	9302

A study of the relative velocities of the cations in those five salts indicates that osmose varies inversely as the velocities of the cation divided by the valence. For instance the velocity of the potassium ion at 18° in $\frac{N}{1000}$ salt solutions is 63.7 and the velocity of the sodium ion is 42.9. The reciprocal of the ratio of the velocity of the sodium ion to that of the potassium ion is 148.4. This value divided by the valence (in this case one) gives 148.4. With a bivalent cation this value must be divided by two.

In column I. of the following table are given the absolute velocities of the cation divided by the valence. In column II. are given one one hundred times the ratios of the velocity of the potassium ion to each of the values in column I. Column III. represents the osmose of the nitrates of these metals at 18° in $\frac{N}{1000}$ solutions on the basis of potassium nitrate, one hundred.

	I. Velocity divided by valence.	II. 100 times velocity ratios.	III. Osmose.
K	63.7	100	100
Na	42.9	148.4	119.5
Li	34	187.3	151
$1/2 \text{ Ba}$	52.2	61	63
$1/2 \text{ Sr}$	48.9	65.1	72

The above values for velocities of cations were made at 18° in $\frac{N}{1000}$ solutions as given in "Leitvermögen der Electrolyte."

The original work of Frazer had for its immediate object the discovery of the salt best suited for removing air by electric

osmose from the walls of porous cells previous to the deposition of semi-permeable membranes.

Since then lithium sulphate has always been used for this cleansing purpose.

In the Spring of 1906 the investigation was taken up by the authors using an apparatus described as "The Drainage Form" and another, differing in principle, to be discussed later.

DRAINAGE FORM OF APPARATUS.

As now used this is an improvement on the Wiedemann form and is easily operated.

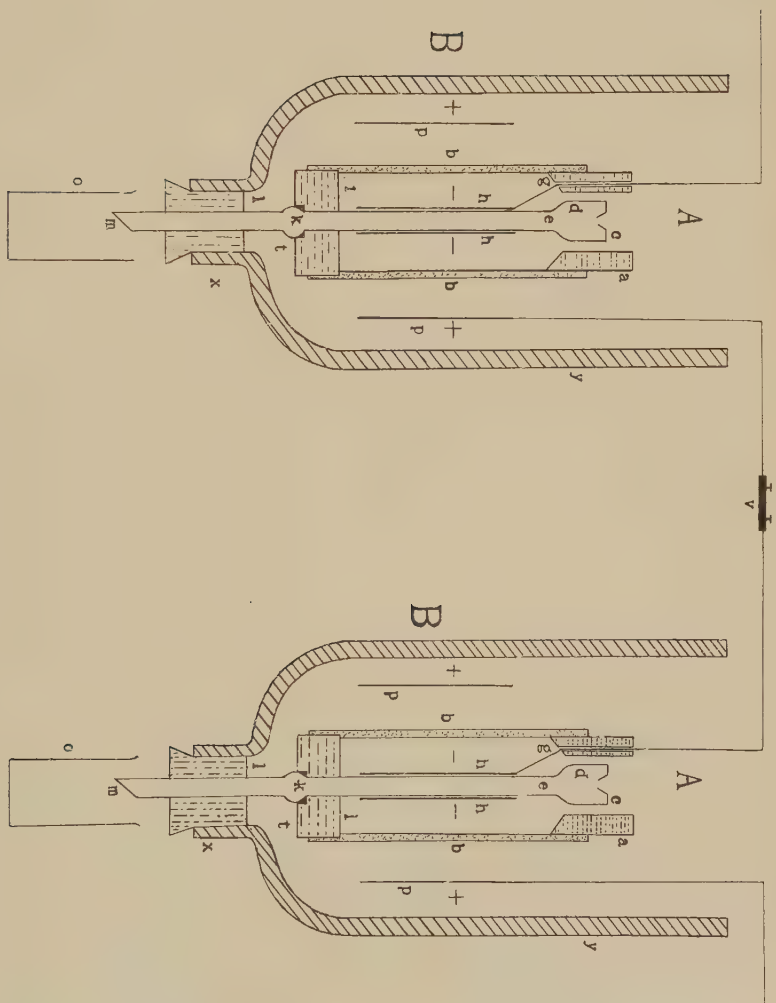
The glass vessel B was made by cutting off the bottom of a half-liter bottle and inverting it as shown in the cut. The bottom of the bottle is used as a cover—the edges having been well ground—to keep out dust and gases. To secure a better joint a wide rubber band is slipped around the line of contact between bottle and cover. The porous clay cell *b* is ground at both ends to hold the soapstone washers *i* and *a*. In the center of *i* is a hole just large enough to allow the entrance of the drainage tube *e*. This tube is enlarged at *k* and the bulb so formed set firmly in the cavity *t* which is then painted with a solution of rubber in carbon bisulphide.

The piece *a* is merely a large cylinder used to constrict the upper part of the cell and *d* is a short piece of rather wide glass tube sealed to *e*. As a result, the space between *d* and *a* is very narrow and a slight increase in the amount of liquid in the porous cell causes a marked rise in the level of the solution. The entire surface of *a* is covered with a smooth coating of a solution of rubber in carbon bisulphide properly vulcanized. The under surface is beveled to prevent the lodgment of air.

The platinum electrode *h* tightly clasps the drainage tube and the wire leading to it passes through *g*. This hole is closed by painting with a solution of rubber in carbon bisulphide. The other electrode *p* is a large cylinder of platinum surrounding *b*.

The tube *e* is ground at a sharp angle at *m* to facilitate dropping.

The two parts, I and II, of this apparatus are exactly alike and are connected in series as shown in the cut. The bottles



rest upon a platform containing two holes just large enough to admit their necks. This platform is simply a shelf in a box, so placed that the tops of the bottles project slightly through the holes in the top of the box. A glass door closes the front of the box and the whole arrangement is planned to keep out dust from the moist cell wall and solution.

The box rests upon a heavy slab of iron placed on four large rubber stoppers each resting in a box full of sawdust. This arrangement lessens the effect of jarring. Vibrations of this sort cause ripples on the surface of the liquid in *b* and irregular drainage in consequence.

The vessel B was filled with solution to a point somewhat higher than *c* and allowed to stand a long time. When the level of the liquid ceased to fall, a mark was etched on the inner surface of B at the surface of the solution. This mark being in the same horizontal plane as *c* indicated the height to which B should be filled in subsequent experiments.

In operating this apparatus B was filled to the mark and *b* filled to overflowing. A platinum disk *c* with serrated edges and the center cut out and prongs bent downward rested on top of *d*. This disk gave a great many points of contact and, as the level of the liquid rose, regulated the overflow.

In the beginning of a series both cells were filled with $\frac{N}{1000}$ potassium nitrate and a current at thirty-six volts passed through both. The solution passed from the anode through the porous wall to the cathode raising the level of the liquid in the porous cell, drained into *d* and dropped into the weighing-bottles *o*. In all the experiments described the tubes were made to overflow just previous to running by pouring a little solution in the porous cell. After standing two minutes, long enough for a clean tube to drain nearly dry, the weighing-bottles were placed under and the current turned on for one minute. The apparatus was allowed to stand for two minutes longer, and the overflow weighed. Of course there was as much water in the drainage tubes before collecting the overflow as after, so the error from this source is small.

When a series of such experiments gave a constant ratio

between the two cells this was used as a correction factor in succeeding experiments where cell I. contained $\frac{N}{1000}$ potassium nitrate and cell II. a different solution.

The natural cell ratio was frequently redetermined and was found to change slowly, due, probably, to the effect of different solutions on No. II.

There are several advantages in this apparatus. The cathode could be so made that it could easily be removed and cleansed when working with solutions depositing metal on this electrode. The other form of apparatus is limited to the use of salts which do not make such metallic deposit, acids and some bases.

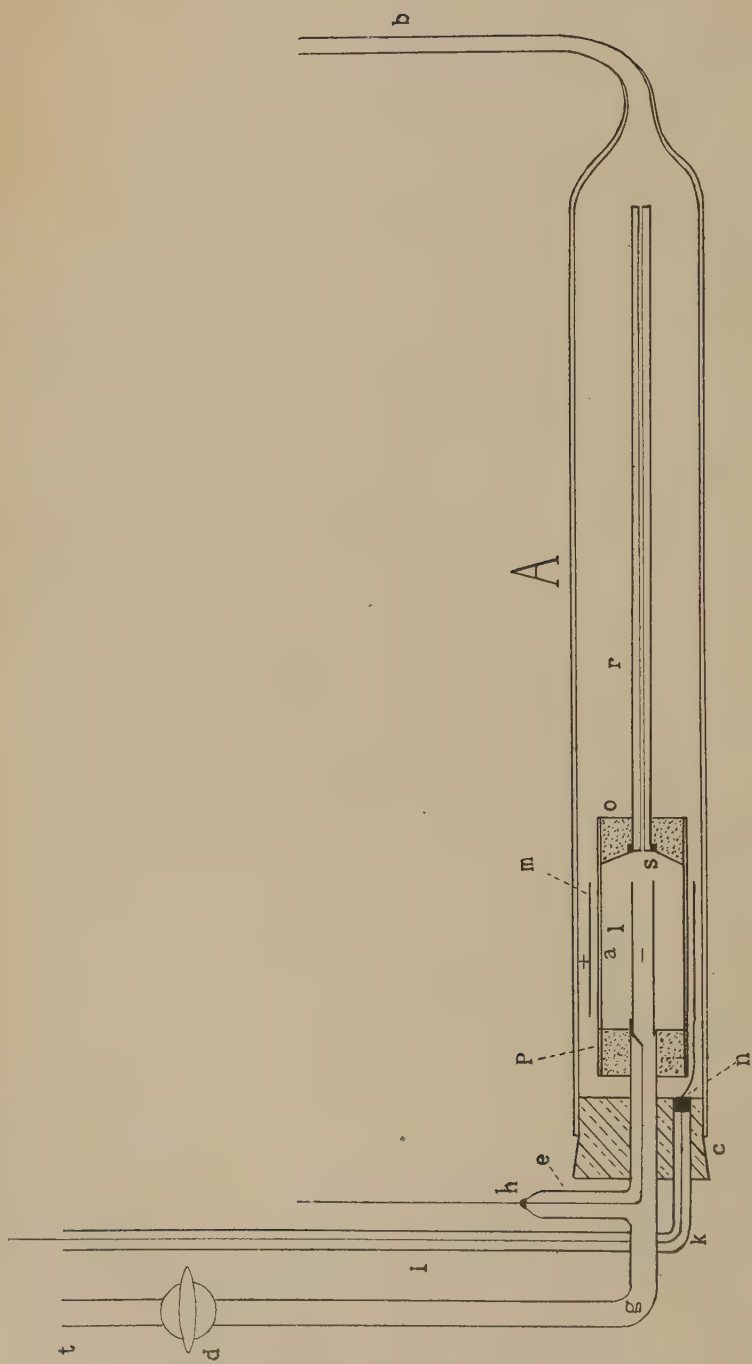
The improved Wiedemann form is easy to operate and readily repaired but, in order to get sufficient osmose to measure, requires many times the electrolysis needed in the Frazer form of apparatus.

The wide top on the drainage tube is of the greatest value in two ways. It narrows the upper part of the cell at the surface of the liquid and affords much more surface for drainage than the narrow tube originally used. In the first experiments of Frazer a U shaped rider of platinum wire was set across d in place of the platinum disk now used. This rider varied so much in its position that glass riders were tried, without success.

Then small caps with serrated edges and perforated center were used with better results. These first caps, however, moved slightly, causing some of the outer points to project beyond the outer surface of d . The effect of this was to allow drainage to continue long enough to cause the level of liquid to fall below its normal height.

Finally caps were cut slightly wider than d , placed between two brass rods also of a greater diameter than d and caps and rods turned on the lathe to the exact diameter of d . The prongs cut in the center of the cap were bent downward and against the inner wall of d so that the cap was held in a fixed position.

So sensitive is this improved apparatus that solution drops



from *m* in five seconds after passing the electric current through the apparatus and stops dropping as quickly at the close of the experiment. The caps and drainage tubes were frequently cleansed with hot chromic acid.

Considering that the weighing-bottles are not open longer than three minutes the loss by evaporation is negligible. Evaporation is checked by the constant presence in the closed box of two beakers of solution which keep the air saturated.

The other form of apparatus used for osmose measurements is represented in the following cut:

The outer glass jacket *A* is drawn out to a narrow neck *b* bent at a right angle. At *c* is inserted as tightly as possible a No. 8, two-hole rubber stopper. Through the central hole passes the glass tube *g* leading into the porous cell *a*. This entrance tube was made by sealing together a tube containing a good stop-cock *d* and a T tube *e* making a right angle bend at *g*. The stem of the T tube is utilized as an exit for the platinum wire leading to the electrode *l* contained in *a*. This stem is sealed at *h* and made water-tight by a drop of fusible glass. A rubber tube fits tightly over the stem of the T tube and contains the platinum wire above mentioned. Through the second hole in the rubber stopper passes a narrow glass tube *i* bent at a right angle at *k*. This holds the platinum wire leading to the platinum anode *m*. At *n* this tube is tightly closed by a soapstone washer set in by a solution of rubber in carbon bisulphide afterwards vulcanized. The cell *a* was made by Morse and Frazer for osmotic pressure measurements and is extremely porous. It is seven centimeters long and about two and a half centimeters in diameter. When mounted on the lathe it was accurately ground for a distance of fifteen millimeters at each end so as to admit the two soapstone washers *o* and *p*.

The washer *p* is plain on both sides but *o* is ground concave on the inside so as to allow all the air to be forced out of the capillary tube *r* when *a* is filled.

After mounting on the lathe a hole is bored in *o* in which the capillary tube fits quite accurately. This hole is enlarged on the inner side of *o* for a depth of five millimeters and the cavity so formed filled with a solution of rubber in carbon

bisulphide after the capillary is set in position. The end of *r* is just flush with the inner surface of *o*.

Both washers are cemented to the cell and the glass tubes passing through them by molten shellac and afterwards heated to a temperature of 125° to drive off the volatile portion of the shellac. Then thin coats of a solution of rubber in carbon bisulphide are applied and the rubber hardened at a temperature of 115° .

The cathode *l* is a sheet of platinum foil about three and a half centimeters long, rolled in the form of a cylinder and inserted for a distance of five millimeters in the end of the glass tube *g*. This keeps it in a fixed position. The anode *m* is a sheet of platinum foil entirely surrounding *a*.

An exact duplicate of this apparatus rested beside it in the water bath and the two were connected in series as in the original form of apparatus used by Frazer. This apparatus is extremely sensitive in results obtained but is easily damaged. Any particles of dirt accidentally falling in the solution may interfere seriously by obstructing the passage of the air bubble index in the capillary tubes. The greatest care has been taken to prevent this and the capillaries were occasionally cleansed by drawing warm chromic acid part way through the tubes, taking precautions not to let the acid reach the porous cell.

At first we used tubes of much larger than capillary bore but this introduced unequal changes in the concentration of different solutions in the duplicate cells and another error mentioned later. The capillaries were graduated in millimeters and accurately calibrated so that the ratio between the volume of No. II. and No. I. might be used to correct the direct readings. The ratio of the volumes of equal lengths of the two capillaries used in this work was 1: 1.05.

The soapstone washers and entrance and exit tubes in each cell were set together with a solution of rubber in carbon bisulphide. The united parts of the apparatus were then dried a few hours at ordinary temperature and later heated at 115° C. The first time this was attempted the apparatus after two weeks' testing developed a leak due to insufficient vulcanization. The rubber turned a light color, showing the effect of the water. Results obtained by this defective apparatus are not quoted.

In remaking the apparatus, care was taken to vulcanize the rubber for several days and, so treated, it remained firm and black indefinitely.

It will be seen that the use of a rubber stopper at *c* gives a tight joint and allows easy access to the cell and capillaries.

The inner electrode was rolled in the form of a cylinder but, as first arranged, this cylinder was so small as to hold air bubbles which could not be dislodged by violent shaking. Air in the porous cell acted as a cushion and caused the index to spring ahead too far and then fall back, making accurate readings difficult or impossible.

The second time the apparatus was made, the platinum cathode was unrolled so as to form a trough of much greater diameter. It was then found that air bubbles were no longer trapped in the cathode. The duplicate parts of the apparatus rested on a platform and were completely covered with water contained in a glass tank. To facilitate reading the position of the index in the capillary, two mirrors were placed in the bath in such positions as to reflect most light on the scale. A common aquarium was used for a bath and readings could be made either through the glass sides or from above. Attempts to use the apparatus in a vertical position were prevented because the index in the capillary caused a difference in the hydrostatic pressure inside and outside the cell which brought about a gradual ascent of the index in the capillary. The open tube *b* maintains atmospheric pressure within the glass jacket *A*.

To fill the cells with solutions the rubber tube attached at *t* is carefully washed with the solution to be used, one end immersed in the solution and the other slipped over the glass tube *g*. The tube *b* is connected with a suction pump by a short piece of rubber tubing which can be closed by a pinch-cock at the proper time. The whole apparatus is held in a vertical position by a clamp stand and the suction applied. All the liquid passes through the cell and out, the capillary forcing out the air. When the level of the liquid is just below the upper end of the capillary, the stop-cock *d* and the pinch-cock are closed and the apparatus, with tubes attached to both ends, carried to the window where a strong light shines on the cap-

illary. Keeping the open end of the capillary always under liquid the pinch-cock is slowly released and air admitted. The apparatus is then held vertically as before, the open end of the capillary up and above the level of liquid, the rubber tube at *t* is held in the mouth and the stop-cock *d* carefully opened. By a slight suction an air bubble of any desired length may be drawn into the capillary, the length being regulated by quickly inclining the tube so as to immerse the open end of *r* in the liquid. The index bubble can then be drawn to any desired position. With a small funnel made by drawing out a piece of wide tubing to a fine stem, the filling of the jacket may be completed.

In practice it was found that a bubble should be about half a centimeter in length. The bubble tends to rise and leave a passage beneath for outflow of liquid. This effect, however, is noticeable only with a very short bubble. In a tube of larger than capillary bore the possibility of error from this source is greater.

Both pieces of apparatus having been filled, they are placed in the bath, the terminals connected in series, the index bubble set near the entrance of the capillary into the porous cell and its position read on the scale to the smallest possible fraction of a millimeter. A movable electric light with reflector attached is a great aid in this reading. The circuit is closed long enough to allow the bubbles to run nearly to the end of the capillaries and immediately on breaking the circuit their position is read as before. This motion of the index away from the cell *a* is observed only when the liquid moves to the negative electrode contained in *a*. On passing the electric current through the apparatus the solution moves into *a* through the pores of the cell wall. The hydrostatic pressure within the cell then drives the air bubble index outward.

The difference between the scale readings taken immediately before and after the passage of the current is the distance traversed by the index. If the diameters of the two capillaries were the same, these distances would represent the relative osmose in the two cells. The tubes used in these experiments were accurately calibrated and the ratios of their volumes found to be 1: 1.05. In all readings correction was made for this difference in volume.

A number of readings were always made without changing the solutions in the cells, by drawing back the bubbles near the cells and closing the circuit as before. The average of these readings is taken as representative of the filling.

Before starting a series of measurements, both cells are filled with the same solution, in the experiments recorded here, $\frac{N}{1000}$

potassium nitrate. A number of fillings are made until a constant ratio between the osmose of the two cells is obtained. This constant ratio is then used to correct the following measurements. One of the cells is selected as a standard and

always contains $\frac{N}{1000}$ potassium nitrate. In the other we place

the solution, for instance $\frac{N}{1000}$ sodium nitrate, whose osmose is

to be measured. After standing a few hours, this latter solution is emptied without closing the circuit and refilled with the same solution as before. At the same time the standard cell

is refilled with $\frac{N}{1000}$ potassium nitrate. Both cells are now

allowed to stand three hours, usually, and then readings taken. Correcting for the difference in the volumes of the capillaries and for natural difference in the osmose of the two cells, the real ratio between the osmose of sodium nitrate and potassium nitrate may be calculated. In all cases a series of fillings are made until the readings are practically constant.

It was found advisable to make as few runnings as possible on each filling because of an apparant electrification of the cell wall which caused great variation in the ratios. Attempts to cleanse the cell wall by continued electrolysis were found inadmissible at an early stage of the work. In one instance a

$\frac{N}{1000}$ solution of barium nitrate, when electrolyzed for some

time with a current at a potential of 110 volts, showed a slight but distinct, negative osmose. After the cell containing the barium nitrate had been refilled with some of the same solution

and allowed to stand several hours, the usual positive osmose was observed on closing the circuit.

Diffusion is now relied on to cleanse the previous solution from the cell wall when a change is made. If solutions are allowed to stand a day there may be sufficient solvent action on the rubber and glass to change the concentrations and, as a result, the ratios. About three hours has been found to be the best length of time to allow the solutions to stand in the apparatus before making a measurement of its osmose.

The natural cell ratio during these experiments was taken immediately before and after running each solution whose osmose was measured.

The salts used were purified by recrystallizing four or five times, and some were dried in an electric bath at proper temperatures, then over phosphorus pentoxide. All were kept in weighing-bottles under a bell jar in which was a plate of phosphorus pentoxide.

All weighings were made from closed weighing-tubes by difference, the salt being quickly transferred from the weighing tube to a 250 cc. flask. This flask was filled to the mark and the calculated number of cubic centimeters run into a clean liter flask, which was filled to the mark with the solvent, giving a solution of any concentration desired. In all experiments described here, conductivity water was used as the solvent.

Practically all the experiments were made with $\frac{N}{1000}$ solutions because the salts were nearly completely dissociated at that concentration, and contamination of the solutions at greater dilutions would introduce too great an error.

The great advantage of connecting the two cells in series is that the same current passes through both solutions and the ratio obtained really gives the relative osmose. In all previous work only one cell was used and successive measurements compared. Here current conditions were not uniform and the ratios so obtained unreliable. Other influences, such as temperature, are the same in both cells in the present method of working and the time of running is identical for both.

The influence of voltage was studied early in this investiga-

tion. It was found that two volts would little more than overcome the friction in the capillary—sometimes the bubble would stop absolutely. Six volts gave variable results for the relative influence of friction was still large. Twelve volts, thirty-six, seventy-five and a hundred and ten were used, all giving concordant ratios.

In Tables I., II., III., IV., V., VI., VII., and VIII. are given the values of the osmose of nitrates of the alkali and alkaline earth metals determined at 18° in $\frac{N}{1000}$ solutions relative to potassium nitrate one hundred. The values found by successive experiments without change of solution are presented and the "mean" of these, considered representative of that "filling". Table IX. gives the average of these mean values for each nitrate.

TABLE I.

RELATIVE OSMOSE OF SODIUM NITRATE.

147.9	147.2	150.5	148.8
147.2	142.7	151.8	150.7
148.4	148.8		149.1
147.8 = mean	147.9 = mean	151.1 = mean	149.5 = mean

TABLE II.

AMMONIUM NITRATE.

103.5	103.2	102.7
102.9	102.5	103.0
103.7	102.3	102.7
103.4 = mean	102.6 = mean	102.8 = mean

The osmose of lithium and caesium nitrates was measured with the drainage apparatus in which the considerable electrolysis makes only one determination with each "filling" possible.

TABLE III.

LITHIUM NITRATE.

184.3
182.8
183.7
179.5

TABLE IV.

CAESIUM NITRATE.

97.6
96.9
95.3

TABLE V.

RUBIDIUM NITRATE.

97.	97.4	97.4	Results from drainage apparatus.
<u>96.8</u>	<u>97.2</u>	<u>98.2</u>	
96.9 = mean	97.3 = mean	97.7 = mean	96.9
			<u>95.7</u>

The osmose of barium, calcium and strontium was measured with the drainage apparatus.

TABLE VI.

BARIUM NITRATE.

61.7
59.6
53.9

TABLE VII.

CALCIUM NITRATE.

62.4
63.6
67.8
65.4

TABLE VIII.

STRONTIUM NITRATE

61.1
58.0
65.0

In column I. of the following table are found the mean values for the osmose of the nitrates of the alkali and alkaline earth metals relative to potassium nitrate one hundred.

Column II. contains values for osmose based on the theory that osmose varies inversely as the velocity of the cation divided by the valence.

Column III. shows the relative specific resistance of $\frac{N}{1000}$ solutions of these metals³ at 18°.

TABLE IX.

	I. Osmose.	II. Theoretical osmose.	III. Relative specific resistance.
KNO_3	100.	100	100.
NaNO_3	149.1	148.4	120.7
NH_4NO_3	102.9	101.6	98.7
LiNO_3	182.6	187.3	139.6
CsNO_3	96.6	95.2	...
RbNO_3	96.9	95.2	...
$1/2 \text{ Ba}(\text{NO}_3)_2$	58.4	61.0	108.9
$1/2 \text{ Ca}(\text{NO}_3)_2$	64.8	66.6	113.8
$1/2 \text{ Sr}(\text{NO}_3)_2$	61.3	65.1	114.3

Table X. gives the relative osmose of different concentrations of potassium nitrate at 18° .

TABLE X.

I. $\frac{N}{2000} \text{ KNO}_3$	II. $\frac{N}{1000} \text{ KNO}_3$	III. $\frac{N}{500} \text{ KNO}_3$
204.6	100	47
205.5	100	47.6
204.4	100	47.9
202.8	100	48.8
203.8	100	47.4
-----	-----	-----
204.2 = mean	100. = mean	47.9 = mean
IV. $\frac{N}{250} \text{ KNO}_3$	V. $\frac{N}{100} \text{ KNO}_3$	VI. $\frac{N}{10} \text{ KNO}_3$
23.6	8.9	0.9
23.8	8.7	0.9
23.7	9.1	1.2
24.5	8.5	1.0
-----	9.0	-----
23.9 = Mean	9.2	1.0 = Mean
	9.0	

	8.9 = Mean	

It can be seen from these figures that osmose varies inversely as the concentration.

Lack of time prevented a quantitative study of the osmose of acids but qualitative measurements were made with $\frac{N}{1000}$ nitric and acetic acids.

Cell I. of the drainage apparatus was filled with $\frac{N}{1000}$ potassium nitrate and cell II. with $\frac{N}{1000}$ nitric acid. On closing the circuit no liquid drained from No. II. although more than usual flowed from No. I. On close examination it was seen that the level of the liquid in the porous cell of No. II. had fallen considerably below *c*, showing that the direction of the osmose was opposite to that observed in all previous experiments. This passage of liquid to the anode may be termed negative osmose, positive osmose having the same direction as the electric current.

To measure the negative osmose of the nitric acid solution the connections with the electrodes of No. II. were interchanged, making the electrode within the porous cell the anode. After refilling the apparatus as before, the circuit was closed and liquid dropped from both drainage tubes. In this and a number of later experiments, the weight of the solution dropping from No. II. was fourteen per cent of that collected from No. I.

The change in direction of the osmose of No. II. makes it impossible to give any value for the natural cell ratio. In other words, there is no way to correct the ratio of weights of liquid collected. An accurate method of comparing positive and negative osmose is yet to be devised.

In another series of experiments, cell I. was again filled with $\frac{N}{1000}$ potassium nitrate and cell II. with $\frac{N}{1000}$ acetic acid. The negative osmose of acetic acid was much greater than that of nitric acid. The weight of solution collected from Cell II. was 1.28 times that collected from cell I. These figures are not to be taken as a basis for exact quantitative comparison of the osmose of nitric and acetic acids but they certainly show that the negative osmose of acetic acid is distinctly greater than that

of nitric acid. By filling Cell I. with a solution of acid selected as the standard of comparison and filling Cell II. with another acid solution of the same concentration, relative negative osmose can be determined and such a series of experiments will be carried out.

RELATED PHENOMENA.

Another phenomenon closely related to osmose is the movement of colloidal particles under the influence of the electric current. This was first observed by Reuss in 1809, and considerable attention has been given to the subject by Quincke and later investigators.

Among the positive colloids or those which migrate to the anode are gold, platinum, arsenic sulphide and indigo. The negative colloids, as Le Blanc terms those which move to the cathode when the circuit is closed, are the hydroxides of iron, aluminium and chromium, hemoglobin, methyl violet and others. Le Blanc¹ states that suspended particles take the place of the glass wall of a capillary, and the difference between the dielectric constants of the particles and solvent influences the direction in which they travel.

Electrostenolysis² is also associated with the phenomenon of electric osmose. Braun observed that when a salt solution separated into two portions by capillaries is electrolyzed a deposition of metal takes place in the capillaries.

The best way to observe this phenomenon is to heat the closed end of a glass tube and quickly plunge it in cold water. The glass shivers into a great number of fine cracks which act as so many very narrow capillaries. An electrode and a solution of a salt are placed in the tube which is set in a vessel containing the same solution and the other electrode. On closing the circuit the osmose through the cracks electrifies the glass to such an extent, in certain cases, that the negative charge on the glass neutralizes the positive charge on the cation and a metallic deposit in the crack is observed.

¹ Le Blanc's *Electro Chemistry*, 157.

² *Zeit. Elektrochemie*, 4, 501 (1898). *Zeit. phys. Chem.*, 25, 651 (1898). *Jour. Am. Chem. Soc.*, 27, 232 (1905).

DISCUSSION OF RESULTS.

Coehn,¹ giving a clear expression to the "double layer" theory of Quincke and Helmholtz, states that osmose increases with increase in the difference between the dielectric constants of the capillary wall and the liquid filling the capillary. His observations are confined to pure solvents and not to solutions. This theory would seem to offer a possible explanation of certain phenomena observed by Quincke, namely, that water in glass capillaries moves to the cathode and turpentine in similar tubes toward the anode when an electric current is passed through the liquid. Water, having the highest dielectric constant, always shows positive osmose but turpentine, having a lower dielectric constant than glass, gives a negative osmose. In the following table all the solvents with a higher dielectric constant than glass have been observed to give positive osmose and those with a lower dielectric constant than glass a negative osmose.

Dielectric constant.		Dielectric constant.	
Water	80.9	Glass	5.6
Glycerin	56.2	Valeric acid	3.06
Ethyl alcohol	25.8	Benzene	2.25
Aniline	7.22	Turpentine	2.23

A careful consideration of the results of this research indicates that the osmose of the solutions studied varies inversely as the velocity of the cation of the substance in solution, divided by the valence. This theory holds very closely for nitrates of the metals of the alkali and alkaline earths groups when the osmose

is measured at 18° in $\frac{N}{1000}$ aqueous solutions.

Further experiments will be necessary to show that the theory holds as well for bases and other salts. The theory was found not to apply to nitric and acetic acid solutions and will probably not hold for an aqueous solution of any acid. Further work may possibly show that there is a close relation between the osmose of solutions of different acids and the velocity of the anions. The anion of nitric acid has a much greater velocity than the anion of acetic acid.

¹ Wied. Ann., 64, 217 (1898).

A much more extended series of experiments must be made to see more clearly the bearing of this work on those theories which have been proposed to account for electric osmose. The results obtained with $\frac{N}{1000}$ aqueous solutions of different salts do

not agree with the deduction of Helmholtz that osmose varies as the specific resistance of the solutions.

However, the views of Kohlrausch¹ on the hydration of the ions suggest a possible theory worth consideration. Kohlrausch thinks it probable that the ions in aqueous solutions are surrounded with an atmosphere of the solvent. The slower ions, lithium for instance, carry with them a relatively large atmosphere. The fact that in solutions containing the slower cations the electrolytic resistance has nearly the same temperature coefficient as the viscosity of water is evidence in favor of the theory of ionic hydration. The larger this shell around each ion the nearer the resistance to its motions approaches the function of solvent on solvent and hence the temperature coefficients above mentioned approach each other with increase in the size of the atmosphere surrounding the ion.

This hypothesis of ionic hydration may have a decided bearing on the phenomenon of electric osmose and must necessarily be considered. Since the slower cations are supposed to carry the larger atmospheres of solvent, in passing through the porous membrane to the cathode they should take with them larger quantities of liquid than the swifter, but less hydrated, cations. In other words, if osmose is due to hydration of the ions and varies directly with it, experiments with different nitrates, for instance, should show that osmose varies inversely as the velocity of the cations.

The measurements discussed in this dissertation show that such a relation exists, except that this ratio must be divided by the valence of the cation. The results are quite in accord with the theory suggested but are not proportional to the specific resistance of different solutions as deduced by Helmholtz.

¹ Proc. Royal Soc., 71, 348.

It is interesting to note that Hittorf¹ stated that electric osmose has no connection with the velocity of the ions.

If the theory of ionic hydration is to be considered in connection with the theory explaining the cause of electric osmose, then the extent to which the anions are hydrated must also be an important factor. The fact that negative osmose was observed in the solutions of nitric and acetic acids appears to be a confirmation of this view and will lead to a more exhaustive study of the question of negative osmose in a manner similar to the way in which positive osmose was measured.

On the same assumption the fact that all authentic records show a positive osmose for aqueous solutions of salts indicates a greater hydration of cation than anion except where hydrogen is the cation. It is to be expected that hydrogen, the swiftest cation, and hydroxyl, the swiftest anion, should be less hydrated than any others.

The investigation described in this dissertation will be continued at an early date.

APPENDIX.

The conductivity water used in this research was prepared by the method adopted by Jones and Mackay,² with some modifications to lessen the cost of purifying. Ordinary distilled water was boiled from a chromic acid solution into a solution of barium hydroxide and redistilled, the steam condensing in a block-tin tube and the conductivity water collected in a Jena glass bottle. The water was protected from ammonia and carbon dioxide in the air by U tubes containing soda lime and calcium chloride. An electric stove furnished the heat, and an asbestos jacket and a clay cylinder, with further protection from hair padding and woolen cloth, saved much energy otherwise wasted.

The water obtained by this method showed a conductivity of 2.5×10^{-6} at 25°. Later an attempt was made to expel most of the carbon dioxide and ammonia by boiling the water for a few minutes in an open flask just previous to filling the still.

¹ Pogg. Ann., 98, 9 (1856).

² Am. Chem. Jour., 19, 91 (1897).

This improved the water to a marked degree, lowering its conductivity to 1.5×10^{-6} at 25° . At zero this conductivity is less than half the value given above.

This still yielded four liters a day with a current of six amperes at a potential of one hundred and ten volts.

BIOGRAPHICAL.

Harry N. Holmes was born in Lawrence County, Pennsylvania, July 10, 1879.

In 1899 he received the Degree of B. S. from Westminster College, New Wilmington, Pennsylvania. During the five years following his graduation he taught Mathematics and Science, for two years in Gallia Academy, Gallipolis, Ohio, and for the three years following in Dixon Academy, Covington, Louisiana.

In October, 1904, he entered the Johns Hopkins University as a graduate student in Chemistry, his subordinate subjects being Physical Chemistry and Physics. During the year 1906-7 he held the position of Laboratory Assistant.

